

AD-A193 489

AN ELECTROCHEMICAL AND UV-VISIBLE
SPECTROELECTROCHEMICAL INVESTIGATION OF (U) UTAH UNIV
SALT LAKE CITY DEPT OF CHEMISTRY S PONS ET AL
30 JUL 86 TR-76 N00014-83-K-0470

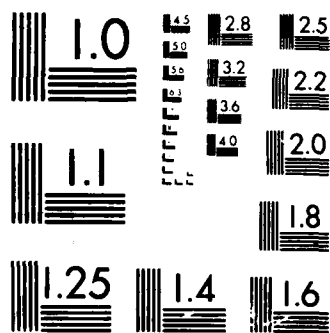
1/1

UNCLASSIFIED

F/G 7/4

NL





AD-A193 489

OFFICE OF NAVAL RESEARCH

Contract N00014-83-K-0470-P00003

Task No. NR 359-718

TECHNICAL REPORT # 76

An Electrochemical and UV-Visible Spectroelectrochemical Investigation
of Selectivity of Potentiometric Gas Sensors Based on Polypyrrole

By

Stanley Pons, K. Ashley, J. Janata, M. Josowicz

Prepared for Publication in
Analytical Chemistry

University of Utah
Department of Chemistry
Salt Lake City, Utah 84112

July 30, 1986

Reproduction in whole or in part is permitted for
any purpose of the United States Government.

This document has been approved for public release
and sale; its distribution is unlimited.

DTIC
ELECTE
APR 14 1988
S H D

88 4 10 068

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
76		
4. TITLE (and Subtitle) An Electrochemical and UV-Visible Spectroelectrochemical Investigation of Selectivity of Potentiometric Gas Sensors Based on Polypyrrole		5. TYPE OF REPORT & PERIOD COVERED Technical Report # 76
7. AUTHOR(s) Stanley Pons, K. Ashley, J. Janata, M. Josowicz		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Utah Department of Chemistry Salt Lake City, UT 84112		8. CONTRACT OR GRANT NUMBER(s) N00014-83-K-0470-P0003
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Chemistry Program - Chemistry Code 472 Arlington, Virginia 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Task No. NR 359-718
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE July 30, 1986
		13. NUMBER OF PAGES
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Conducting Polymers, Potentiometric Sensors		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The sensitivity and stability of polypyrrole as a function of several experimental parameters is discussed.		

Final Exam

AN ELECTROCHEMICAL AND UV-VISIBLE SPECTROELECTROCHEMICAL
INVESTIGATION OF SELECTIVITY OF POTENTIOMETRIC GAS SENSORS BASED ON
POLYPYRROLE

Mira Josowicz† and Jiří Janata*

Department of Bioengineering, University of Utah, Salt Lake City, Utah 84112

Kevin Ashley and Stanley Pons

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

† Present Address: Universitat der Bundeswehr Munchen, D-8014 Neubiberg, West Germany

* To whom correspondence regarding this manuscript should be addressed

It has been shown in previously [1, 2] that a suspended gate field transistor (SGFET) can be used as a general device for sensing of gases and dielectric fluids. The principles of operation of this device is based on chemical modification of the electron work function of a chemically selective layer which is electrochemically deposited within the gate structure of the device.

Electropolymerized polypyrrole (PP), one such layer, can be used as a general matrix into which other chemical functionalities can be incorporated in order to change its selectivity. It has been shown that other organic compounds can be incorporated electrochemically into the bulk of the PP film [3] or that its surface can be covalently modified [4]. Furthermore, PP forms an ohmic junction at noble metal electrodes [5] which is important for the proper operation of the device [1]. In this paper we shall describe the correlation between the spectroelectrochemical characteristics of various types of layers based on PP with their sensitivity and selectivity to some aromatic and hydrogen bonding compounds that interact with the film by hydrogen bonding or through aromatic π -systems.

While pyrrole undergoes slow oxidation at room temperature and atmospheric pressure [6], polypyrrole with BF_4^- anion is remarkably stable after the initial reaction with air. Practically no thermal degradation of the PP has been observed below 130°C [7]. This means that, if necessary, these devices could be used even at moderately elevated temperatures. In this study the operating temperature of the transistor was only 25°C .

EXPERIMENTAL SECTION

Suspended gate transistors with an approximately 2000 Å gap were fabricated and encapsulated as described previously [1]. Encapsulated devices were first etched in solution containing 15 ml (30%) H_2O_2 , 50 ml 0.1M EDTA , and 10 ml conc. NH_4OH for 10 minutes in order to remove traces of residual titanium and tungsten from all surfaces within the gate. Before electrodeposition the Pt gate was conditioned electrochemically by cycling between -0.25 and +1.25 V at 10 V s^{-1} in 1M H_2SO_4 for 10 minutes. Cyclic voltammograms obtained after this pre-treatment were identical with those described by Arvia et.al. [8]. After this step the devices were dried in an oven at 60°C for 12 hours.

The electrodeposition was carried out by applying current pulses supplied from an IBM EC 225 potentiostat operated in the normal pulse mode. The repetition rate was set at 5 seconds, the pulse amplitude was 100 mV, and the scan rate 10 mV/s, the initial and final potentials were +0.6 and +0.9V, respectively unless specified otherwise. The deposition current was integrated with an analog integrator (constructed in these laboratories) until a total charge of $10 \mu\text{C/gate}$ had been passed. In all experiments the reference electrode was Ag/0.1M AgNO_3 in acetonitrile and the basic reaction solution was 0.1 M pyrrole with 0.1M tetraethylammonium tetrafluoroborate (TEAF) as the supporting electrolyte.

Threshold voltage shifts and the basic transistor characteristics were measured with a Hewlett Packard Semiconductor Parameter Analyzer, Model 4145A. Chemical response measurements were made in constant current mode, in saturation ($V_{\text{DS}} = 4.0\text{V}$ and $I_{\text{DS}} = 280 - 350 \mu\text{A}$).

The test chamber was attached to the outlet of a Perkin Elmer Sigma 2000 gas chromatograph and was maintained at room temperature. The carrier gas was nitrogen (typical flow rate was 25 ml min^{-1}). The output from the SGFET monitor was digitized and stored in a Perkin Elmer 7500



Availability Codes		
Avail and/or		
Special		
A-1		

Professional Computer equipped with a LCI-100 Laboratory Integrator.

For the spectroelectrochemical experiments the aforementioned polymers were electrodeposited in the same manner as described above (for Pt wire electrodes) onto 7 mm diameter platinum disc mirror electrodes. These polymer modified electrodes were mounted in a spectroelectrochemical kinetic cell as described previously [9]. Reflectance spectroelectrochemical spectra were obtained for the films using the modulated specular reflectance spectroscopic (MSRS) method [9]. The procedure involved pulse modulation between two potentials at which reactions take place at two different rates. The potential pulse modulation at 40 Hz was supplied by a fast rise-time, three-electrode potentiostat and waveform generator (JAS Instruments), ~~was 40 Hz~~. The resulting reflectance change was monitored with a phase sensitive detector (Bentham). The wavelength was scanned throughout the UV-visible region using a Xenon arc source (Photon Technology International) and a monochromator (GCA McPherson 300). The resulting difference spectra (detected by a photomultiplier, RCA 31000A) were recorded on a plotter. Negative bands correspond to absorbing species present at the higher potential, while positive bands are indicative of absorbers prevalent at the lower base potential.

An MSRS spectrum of the nitrobenzene radical anion was also recorded for reference. The base potential was first held at a voltage where no faradaic process occurred, and then stepped to a value where nitrobenzene was reduced to its radical anion at a diffusion-limited rate. The difference spectrum was recorded as was previously described for the polymer films.

RESULTS

Electrochemistry

Suspended gate field effect transistors (SGFET) coated with polypyrroles (PP) prepared under different conditions have shown markedly different selectivities to various gases, and a large variation in the threshold voltage shift DV_T which is related to the change in the electron work function of the polypyrrole layer [1]. The threshold voltage shifts for SGFETs with various PP layers measured with respect to bare, cleaned Pt in air at room temperature are summarized in Table I together with a qualitative description of their selectivity. In order to characterize these films, we have used both cyclic voltammetry and spectroelectrochemistry. The cyclic voltammograms for PP co-deposited with 4-nitrotoluene, and with nitrobenzene are shown in Fig. 1. It is interesting to note that the voltammetry corresponding to the reduction/oxidation of the nitro group can be seen in nitrotoluenes (only 4-nitrotoluene is shown in Fig. 1A) even after repeated cycling between the reduced and oxidized form of PP. The results are similar to the reduction of poly(N--p-nitrophenyl pyrrole) investigated by Diaz et.al. [4]. The V_T shifts of PP/nitrotoluenes are strongly positive ($\sim +8V$) indicating a substantially increased electron affinity of this material as compared with ordinary PP. On the other hand the V_T shift for the PP/nitrobenzene is only moderately positive and the redox pattern of the nitro group in PP/nitrobenzene can be seen only if the cycling is limited to between 0 and -2.5V (Fig. 1Ba). When the PP is oxidized the nitro group redox pattern is lost after only a few cycles (Fig. 1Bb).

Spectroelectrochemistry

MSRS spectra for the five films are shown in Figure 2; These spectra were taken in 0.1M TBAF/acetonitrile. In each case the recording with reference to a pulse sequence -0.60V to -2.40V

(vs. $\text{Ag}(\text{Ag}^+)$), secondly -0.60V to $+1.20\text{V}$, and thirdly -0.60V to -2.40V , again. This sequence was chosen in an effort to determine differences in the films caused by film oxidation. First the films were reduced, and difference spectra at 40 Hz modulation were recorded. The spectra for the oxidations were then recorded. Finally, the spectra for the reductions were again obtained, and any changes in bands due to film alteration caused by oxidation were noted.

The difference spectrum resulting from the reduction of PP/nitrobenzene film (Figure 2a) differs from those obtained for the other four films; a negative peak at 395 nm appears in the nitrobenzene/polypyrrole spectrum. The difference spectra for the oxidations of the five films are all quite similar (Figure 2b). Subsequent to oxidation, spectra for reductions were again recorded (Figure 2c). The spectra for the five films then appeared similar. The negative peak at 395 nm in the nitrobenzene/polypyrrole film has disappeared as a consequence of the oxidation excursions undergone during the recording of the spectrum in Figure 2b.

The MSRS spectrum of nitrobenzene radical anion is shown in Figure 2 (insert). A single negative Lorentzian shaped peak is seen with a maximum in acetonitrile at 447 nm , somewhat shifted from the maxima seen in DMF [10] and sulfolane [11], where peaks due to nitrobenzene anion radical were observed at 464 and 465 nm , respectively. Neutral nitrobenzene does not absorb in this wavelength region.

Chemical Response

The overall response of the SGFET coated with PP or nitroarene modified polypyrroles parallels the electrochemical observations; All transistors with PP matrix respond to alcohols and to acetonitrile. However, the polarity of the response to acetonitrile as well as its amplitude varies for different PP (Fig.3). The response to methanol is always higher than to acetonitrile; however, the response is somewhat affected by the solvent used for the electrodeposition (Fig.4). For PP deposited from acetonitrile the ratio of response to methanol/acetonitrile mixture is 5.2 whereas for

PP deposited from methanol this ratio is 8.0. The effect of nitroarene co-deposition on selectivity to aromatic compounds is pronounced (Fig.5). While there is no sensitivity to toluene from PP deposited from methanol, acetonitrile, or acetonitrile/1M toluene solutions, both 2-nitro- and 4-nitrotoluene PP give a strong, reversible response, while PP/3-nitrotoluene yields only a weak, irreversible response.

Response of SGFET coated with PP/nitrobenzene depend on the electrochemical history of this material. The PP/nitrobenzene deposited with the final potential at ± 0 V (Fig. 6A) yields a response to water, alcohols, and to the aromatics. Reduced material (Fig. 6B,C) shows a much lower response to aromatics and a lower and inverted response to water. This behavior can be explained by the loss of nitrobenzene from the PP matrix upon reduction of the nitro group. As expected, none of the tested coatings listed in Table I responded to aliphatic hydrocarbons or to cyclohexane.

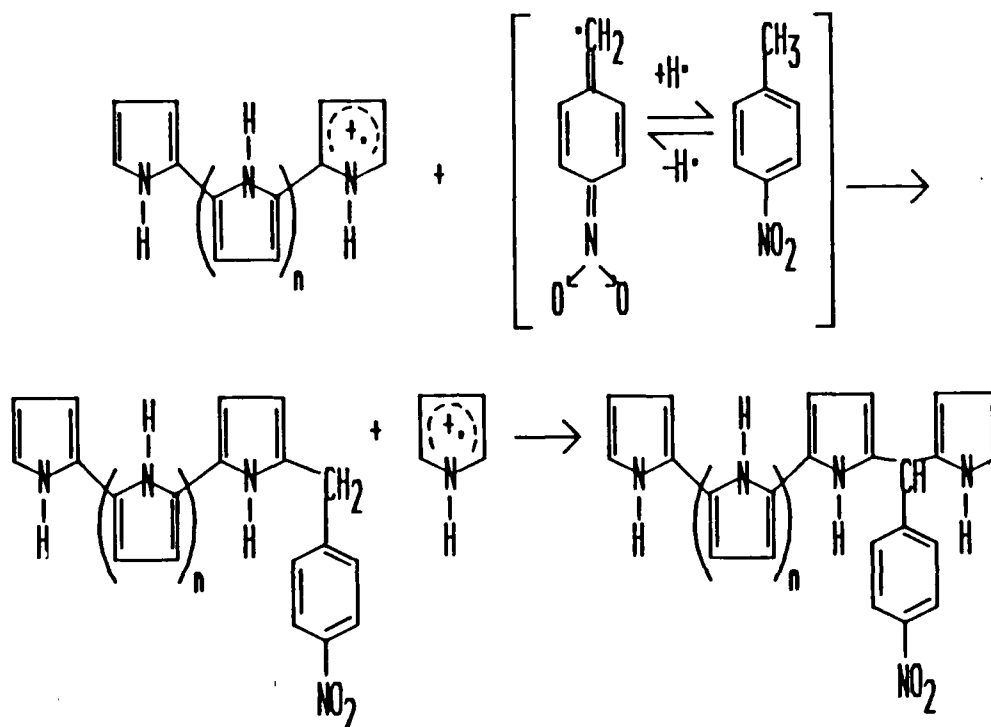
DISCUSSION

The most striking feature of the transistors modified with PP/nitrotoluenes is the large (+6.5 to +8.7V) shift of the threshold voltage (Table I) which indicates a large increase in the electron work function due to the presence of the covalently bound nitroarene moiety. Because of the complex geometry of the transistor gate (Pt mesh) and the resulting non-homogeneous electric field in the gap, no absolute equilibrium measurements have been attempted in this work. However, the rapid return of the signal to the baseline (Figures 3-6) following the passage of the concentration impulse is a clear indication of the reversibility of these interactions. The exception seems to be the response of PP/3-nitrotoluene to toluene which is irreversible (curve c in Fig. 5).

In this group of sensors, PP is used only as a binding matrix, but we see that the chemical selectivity is achieved by incorporation of additional functional groups. As has been observed previously, SGFETs with PP layers respond to alcohols and water. This selectivity is undoubtedly related to the tendency of pyrrole to hydrogen bond [12]. Not surprisingly, all transistors investigated in this study have shown a response to aliphatic alcohols and to water. The fact that the response to water was stronger when the electrodeposition of PP was carried out from methanol rather than from acetonitrile (Fig. 4) indicates that solvation during the polymerization may have left the final polymer with "solvent footprints" which made it an entropically more favorable binder for the organic substrate of similar shape. This may be termed a solvent-induced template effect similar to one proposed for example by Shea and Dougherty [13] for template-mediated synthesis. In this context the PP may not be an optimum matrix because of its high crystallinity [14]. The negative shift of V_T to addition of acetonitrile vapor is consistent with the negative $ΔV_T$ of PP deposited from acetonitrile solution (relative to PP deposited from methanol). The origin of this shift is again presumably in the $π-π$ or $π-H$ interactions between acetonitrile and PP.

The co-polymerization of PP with nitrotoluenes produced a remarkably strong shift in the threshold voltage of the final material as compared to the plain PP (+ 6.787 V for 2-nitrotoluene, +

8.984 V for 3-nitrotoluene and + 7.784 V for 4-nitrotoluene). Such large shifts can be explained only by copolymerization of pyrrole with nitrotoluene and formation of a substantially different material with much higher electron affinity. The likely mechanism for this reaction involves the nitrotoluy radical, analogous to the reaction between pyrrole and benzyl radical [15]:



The presence of incorporated nitroarene has been confirmed by cyclic voltammetry (Fig.1) and by spectroelectrochemistry (Fig.2). On the other hand nitrobenzene, which cannot readily co-polymerize with PP, was found to bind only loosely, presumably as a charge transfer complex with the neutral PP. Upon oxidation of the matrix the nitrobenzene is rapidly lost by diffusion with concomittant loss of sensitivity to aromatic analytes (Fig.6). The sensitivity to aromatic hydrocarbons and the total lack of sensitivity to cyclohexane is due to the π - π interactions of the former with the nitroarene moiety within the PP/nitrotoluene copolymer. The polarity of the response, i.e. induced increase or decrease of the electron affinity is difficult to explain at present, and is the subject of further study.

The electropolymerization of PP is a convenient yet chemically complicated process in which different materials are formed depending on the current density and on the solvent and anion present in the solution during electrolysis [16]. Unfortunately the mesh structure of our suspended gate transistor does not allow us to control the current density such that the exact PP film thickness or a film of uniform chemical composition could be produced. These studies as well as the equilibrium response measurements will be done on SGFET with a parallel plate configuration of the suspended gate.

The MSRS spectra clearly indicate the incorporation of nitrotoluenes into polypyrrole. The difference spectra of the three nitrotoluene/polypyrrole aggregates resemble the spectra obtained from polypyrrole electrodeposited in the absence of any nitroarene (Figure 2). As a result of the initial film reduction (Figure 2a), a positive peak at 440 nm, corresponding to the interband transition in neutral polypyrrole [7], appears in the difference spectra of the three nitrotoluene/polypyrrole films as well as in the spectrum of the polypyrrole film itself. Also, a broad negative peak at around 550 nm, due to the reduced form of the polymer, is seen for all five films. During film oxidation, a very broad positive peak with a maximum near 600 nm is observed for all five films, along with a shoulder near 430 nm. The shoulder corresponds to interband transitions seen above during film reduction. The broad, humped peak with its maximum around 600 nm, is due to transitions in the neutral polymer matrix as well, and probably owes its broadness and structure to the presence of oligomers of varying chain length. Spectral dependence on chain length has been noted before for polypyrrole [17] and in poly-paraphenylene [18]

The magnitude of the peak at 600 nm (Figure 2b) larger than expected is due to the fact that the oxidized form of the polymer is conductive and therefore acts optically more like a metal. Since what is recorded is a difference spectrum, the small absorbances in the visible range due to the neutral species translate into bands of large magnitude when compared with the near zero absorbance occurring at the electrode surface of the oxidized form of the film. The 430-440 nm band is depressed

relative to the 580-620 nm band since the oxidized form of the polymer absorbs to some extent at these higher energies [17]. This is indicated in the difference spectra. No peak due to the oxidized form appears at any wavelength. However, a small contribution to the absorbance in the violet cut-off region due to transitions in the oxidized species cancels to some extent the band due to the neutral form of PP in the 430-440 region.

The difference spectrum obtained during the initial reduction of PP/ nitrobenzene (recorded prior to any oxidation) shows the only optical anomaly (Figure 2a); A negative peak around 400 nm is observed, with the positive peak due to the neutral form of the polymer matrix is absent. No such phenomena appears in the MSRS spectra of the other four polymer films. The spectrum of nitrobenzene radical anion in acetonitrile (Figure 2a-insert) shows a broad peak with a maximum near where the interband transition in the neutral form of PP occurs. It is presumed that the signal due to nitrobenzene radical anion formed during the reduction of surface adsorbed nitrobenzene overwhelms the absorbance due to the interband transition, which is opposite in sign. This accounts for the apparent negative peak at 345 nm and the absence of a positive peak at 440 nm; both nitrobenzene radical and neutral PP absorb in the same wavelength region, and a competition is established which results in the more complex difference spectrum (Figure 2c). The second reduction (Figure 2c) following oxidation (Figure 2b) results in the disappearance of the nitrobenzene anion radical peak, with the appearance of some positive $\Delta R/R$ contribution from the 430-440 nm interband transition band of the neutral species. The spectrum from PP/nitrobenzene is now similar in appearance to the spectra obtained for the other four films. This is evidence that the charge-transfer complex between nitrobenzene and PP postulated previously is probably destroyed when the film is oxidized. Here, spectral information complements voltammetric data (Figure 1) suggesting that nitrobenzene is not incorporated into the polymer during electropolymerization, whereas the three nitrotoluene species do indeed co-polymerize with pyrrole to form the PP matrix.

REFERENCES

1. Josowicz, M.; Janata, J. *Anal.Chem.* **1986**, *58*, 514-517
2. Cassidy, J.; Pons, S. Janata, J. *Anal.Chem.* **1986**, *58*, in print
3. Bull, R.A.; Fan, F.-R.; Bard, A.J. *J.Electrochem.Soc.* **1984**, *131*, 687-689
4. Salmon, M.; Martinez, A.; Kanazawa, K.K. *J.Electroanal.Chem.* **1981**, *130*, 181-187
5. Inganas, O.; Lundstrom, I. *Synt.Metals* **1984**, *10*, 5-12
6. Atkinson, R.; Aschmann, S.M.; Wiener, A.M.; Carter, W.P.L. *Atm. Envir.* **1984**, *18*, 2105-2107
7. Kanazawa, K.K.; Diaz, A.F.; Krounbi, M.T.; Street, G.B. *Synt.Metals* **1981**, *4*, 119-130
8. Cervino, R.M.; Triaca, W.E.; Arvia, A.J. *J.Electroanal.Chem.* **1985**, *182*, 51-60
9. Pons, S.; Khoo, S.B. *J. Am. Chem. Soc.* **1982**, *104*, 3845-3851
10. Kalyanaraman, V.; Dua, S.S.; Rao, C.N.R.; George, M.V. *Tetrahedron Lett.* **1968**, 235-238
11. Armstrong, N.R.; Vandenberg, N.E.; Quinn, R.K. *J.Phys.Chem.* **1976**, *80*, 2740-2744
12. Jones, R.A.; Bean, G.P. *The Chemistry of Pyrroles*, Academic Press, 1977, New York, p.442
13. Shea, K.J.; Dougherty, T.K. *J.Am.Chem.Soc.* **1986**, *108*, 1091-1093
14. Street, G.B.; Clarke, T.C.; Geiss, R.H.; Lee, V.Y.; Nazzari, A.; Pfluger, P.; Scott, J.C. *J.de phys.* **1983**, *44*, C3, 599-606
15. Bass, K.C.; Nababsing, P. *Chem.Ind.* **1974**, 574-576
16. Prejza, J.; Lundstrom, I.; Skotheim, T.; *J.Electrochem.Soc.* **1982**, *129*, 1685-1689
17. Genies, E.M.; Bidan, G.; Diaz, A.F. *J.Electroanal.Chem.* **1983**, *149*, 101-113
18. McAleer, J.F.; Ashley, K.; Smith, J.J.; Bandyopadhyay, S. Ghorogchian, J. Eyring, E.M.; Pons, S.; Mark, H.B.; Dunmore, G. *J.Molecular Electron.*, in press

ACKNOWLEDGEMENTS

We would like to thank Professor V. Horak for helpful discussions and to the Perkin Elmer Corporation for their donation of the laboratory computer used in this work.

CREDITS

This work was partially supported by the Office of Naval Research. One of us (M.J.) wishes to thank the Humboldt Foundation for the Feodor Lynnen Fellowship

FIGURE LEGENDS

Fig. 1 Electrochemical behavior of PP/nitroarene layers prepared on Pt disc electrode (3 cm^2) from 1M nitroarene, 0.1M pyrrole, 0.1M TEA TFB acetonitrile solution. After deposition the electrode was rinsed and transferred to fresh 0.1M TEA TFB actonitrile solution. The scan rate was 0.5 V s^{-1} .

A: PP/ 4-nitrotoluene; B: PP/nitrobenzene cycled first (Fig.1 Ba) between ± 0 and -2.4 V , then (Fig. 1Bb) between 0 and $+1.3 \text{ V}$; C: The first cycle between $+1.3$ and -2.4 V for PP/nitrobenzene. The scan direction is indicated by arrows.

Fig. 2 MSRS spectra resulting from reductive and oxidative pulsing for ----- PP, PP/2-nitrotoluene; - · - · - PP/3-nitrotoluene; - " - " - PP/4-nitrotoluene, and ——— PP/nitrobenzene. Spectrum "nb" is that of solution nitrobenzene radical anion.(a), initial reduction; base potential: -0.60 V , pulse height: -1.80 V . (b), oxidation; base potential: -0.60 V , pulse height: $+1.80 \text{ V}$. (c), reduction spectra recorded after film oxidation; base potential -0.60 V , pulse height: -1.80 V . Sensitivity in (a) and (c) is five times that of (b). Other parameters are given in the text.

Fig. 3 Response to acetonitrile of SGFET coated with various PP. a- PP/4-nitrotoluene; b- PP/2-nitrotoluene; c- PP/3-nitrotoluene; d- PP from acetonitrile; e- PP from methanol; f- PP/nitrobenzene; g- PP/toluene

Fig. 4 Response of polypyrrole deposited from : A - methanol, B - acetonitrile, to injection of $5 \mu\text{L}$ of methanol: acetonitrile mixture (1:10 molar ratio). Nitrogen flow was 24 mL min^{-1} ; $V_{DS} = 4.0\text{V}$; $I_{DS} = 350 \mu\text{A}$

Fig. 5 Response to toluene of SGFET coated with various PP. a- PP/4-nitrotoluene; b- PP/2-nitrotoluene; c- PP/3-nitrotoluene; d- PP from acetonitrile; e- PP from methanol; f- PP/nitrobenzene; g- PP/toluene

Fig. 6 Response of SGFET coated with PP/nitrobenzene in acetonitrile to injection of 0.5 μL of : 1 - acetonitrile; 2 - benzene; 3 - toluene; 4 - methanol; 5 - 0.1 μL of water.

A: Final deposition potential ± 0 V

B: After reduction at -1.0 V for 10 min

C: After repeated cycling between ± 0 and - 2.5 V

ABSTRACT

It is shown that electrochemical incorporation of nitrotoluenes into the the polypyrrole matrix changes profoundly the electron work function of ~~this material~~ as compared with plain polypyrrole. Simultaneously this material exhibits selective sensitivity to aromatic compounds. The presence of the nitroarenes in the polypyrrole matrix has been confirmed spectroelectrochemically.

BRIEF

Selectivity of suspended gate field effect transistors to aromatic compounds, acetonitrile, alcohols, and water can be modified by electrochemical incorporation of different compounds into the polypyrrole layer within the transistor structure.

Threshold voltage shifts and Responses of SGFETs With Polypyrrole Film Deposited Under Different Conditions

Deposition Conditions	V_T Shift	Response
acetonitrile (Ac)	- 0.284	Ac (-)
methanol	+ 0.776	Ac (-)
1M toluene (T), Ac	+ 0.275	Ac (+)
1M nitrobenzene, Ac	+ 0.712	Ac (++)
1M 2-nitrotoluene, Ac	+ 6.503	Ac (++), T (++++)
1M 3-nitrotoluene, Ac	+ 8.700	Ac (++), T(+)
1M 4-nitrotoluene, Ac	+ 7.500	Ac (----), T (---)

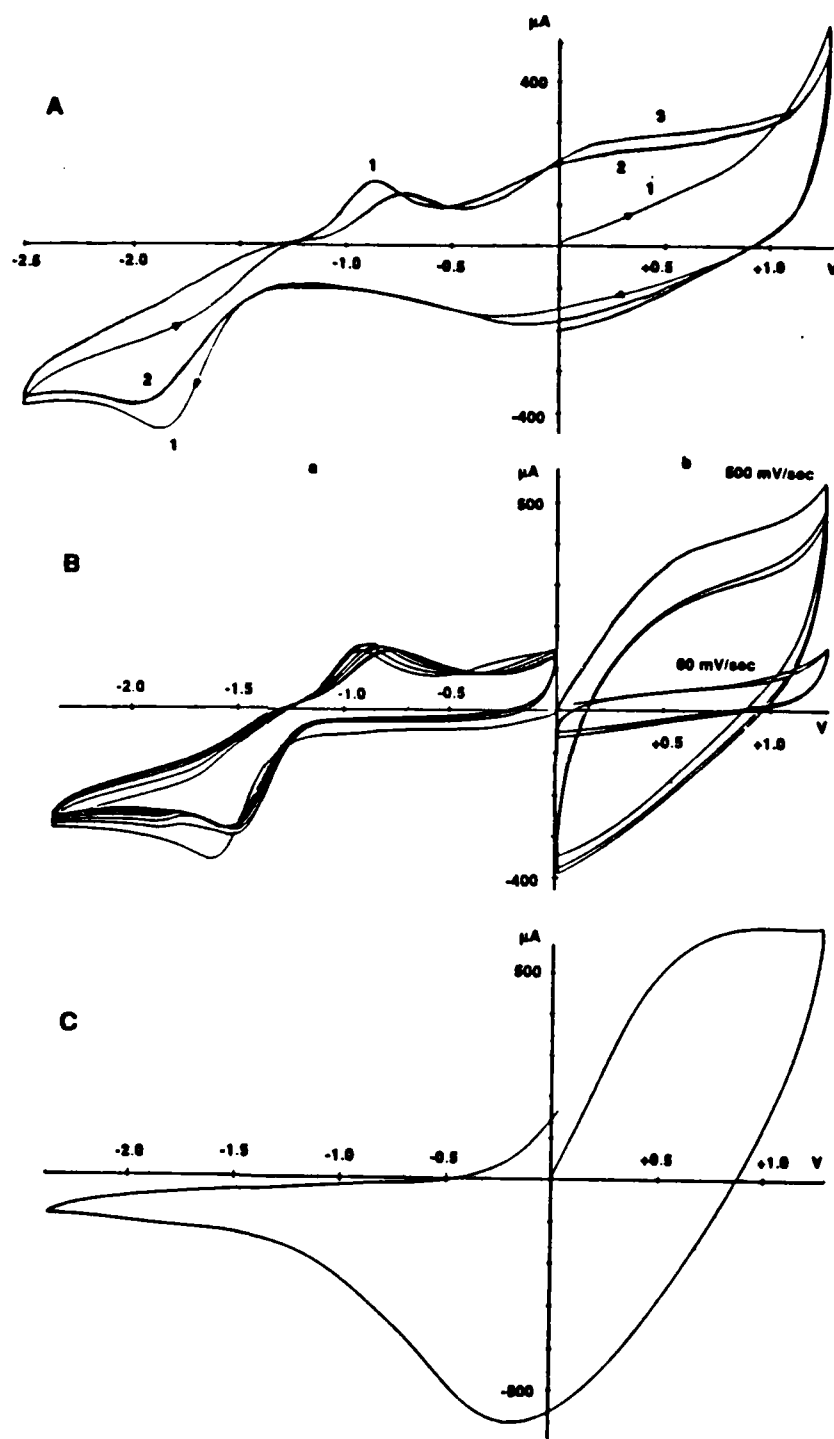


Fig. 1

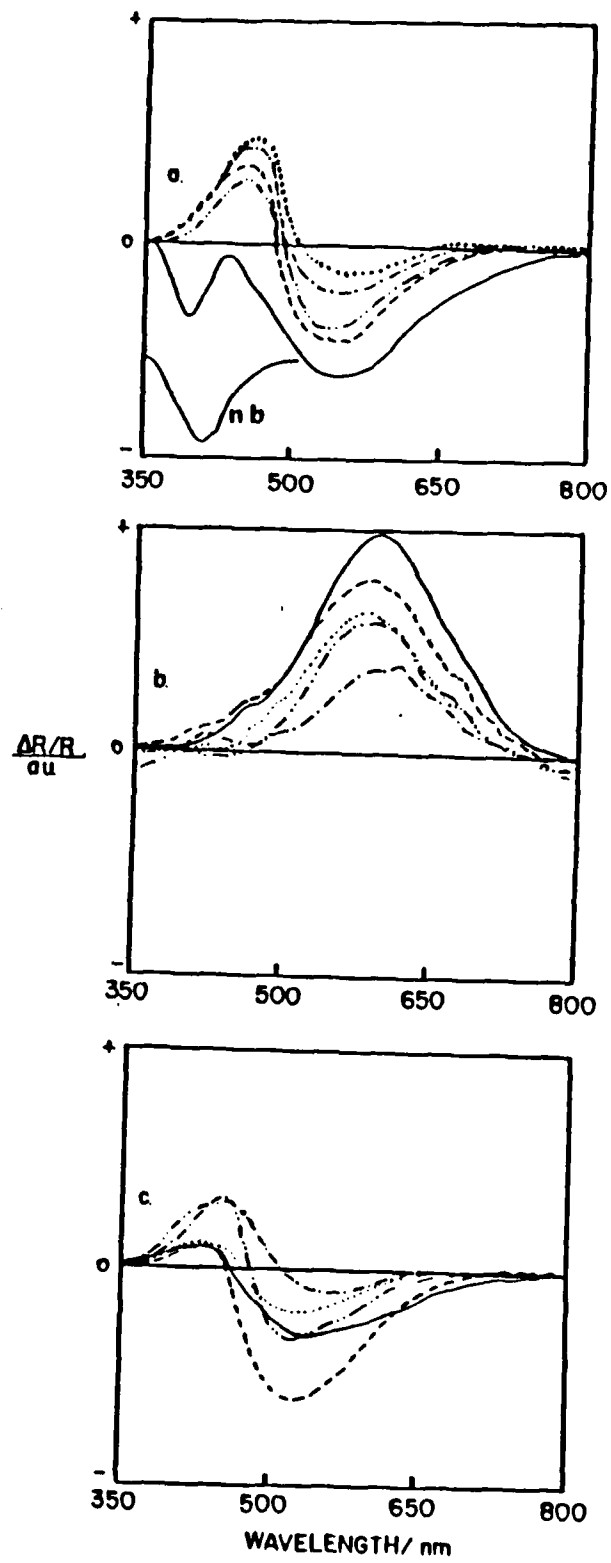


Fig. 2

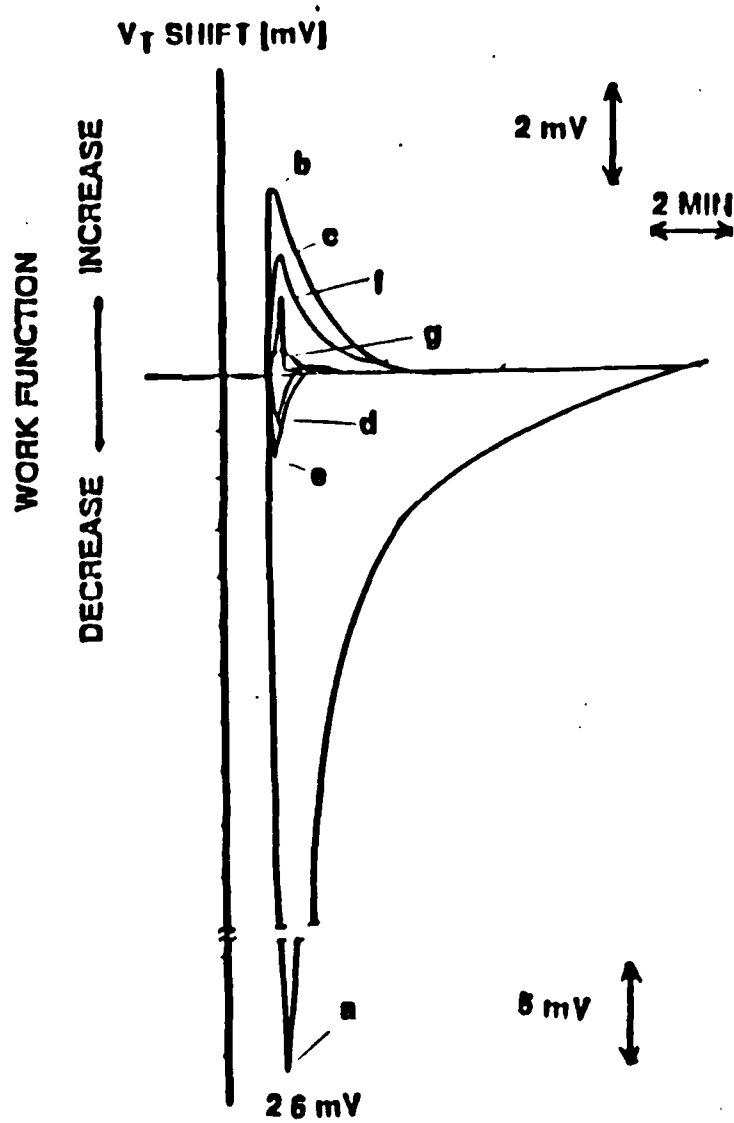


Fig. 3

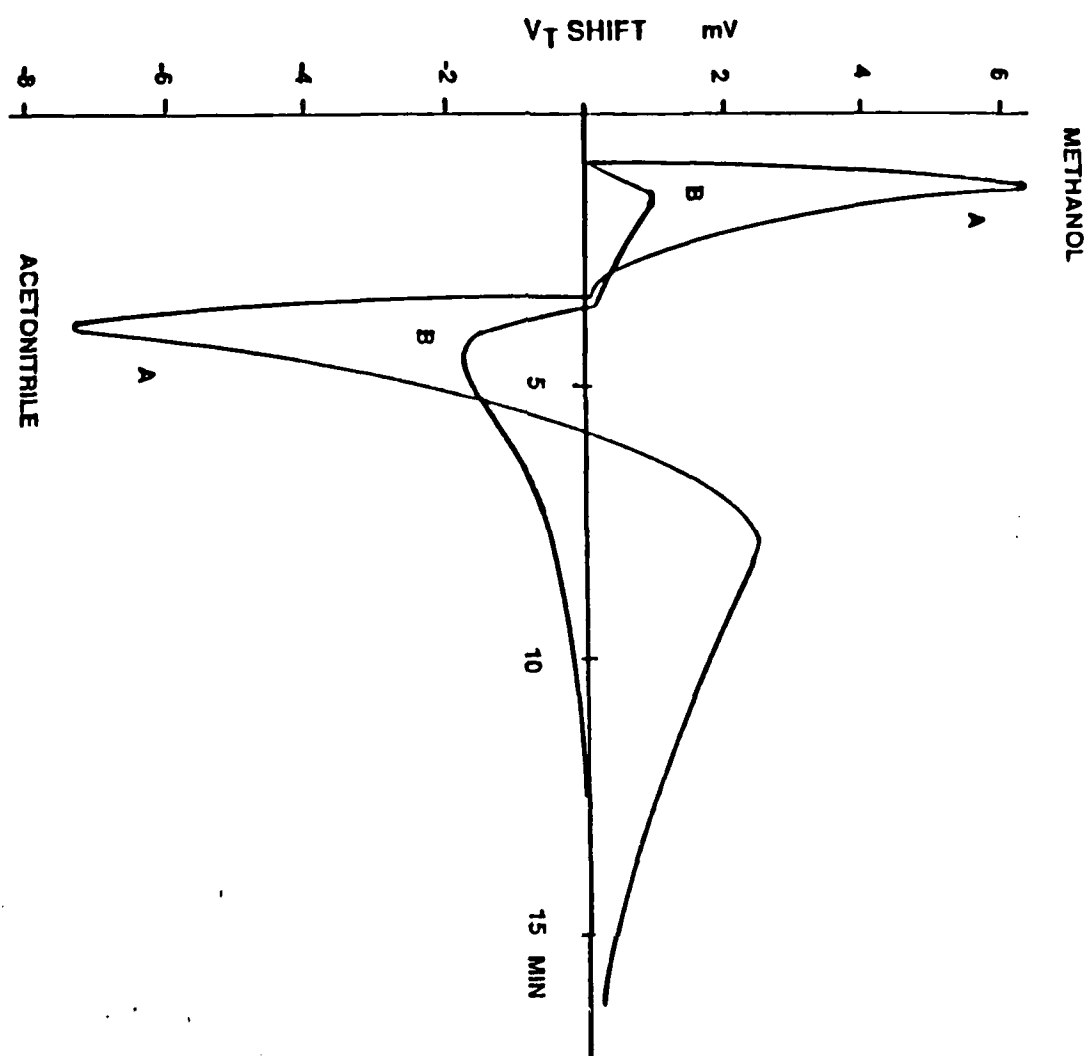


Fig. 4

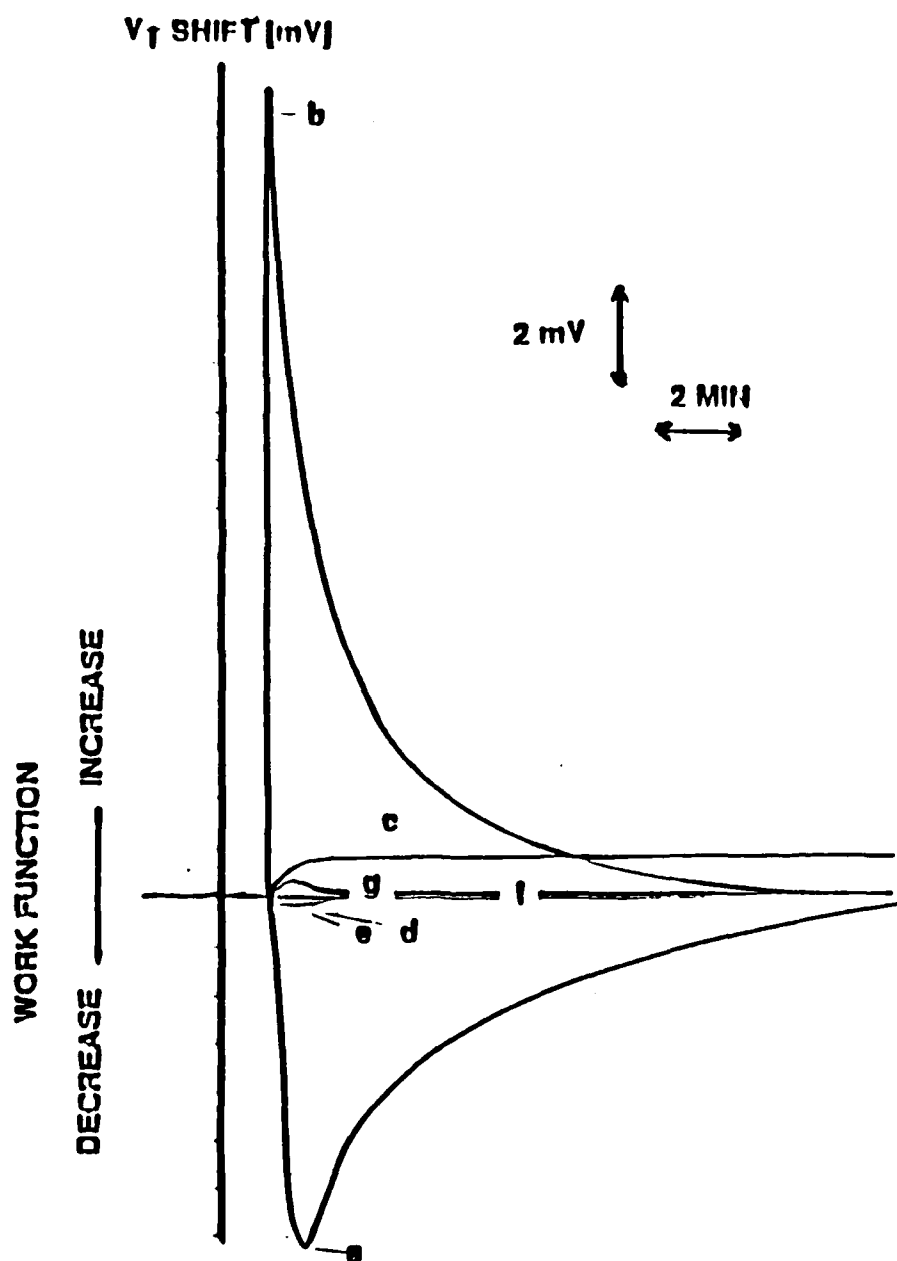


Fig. 5

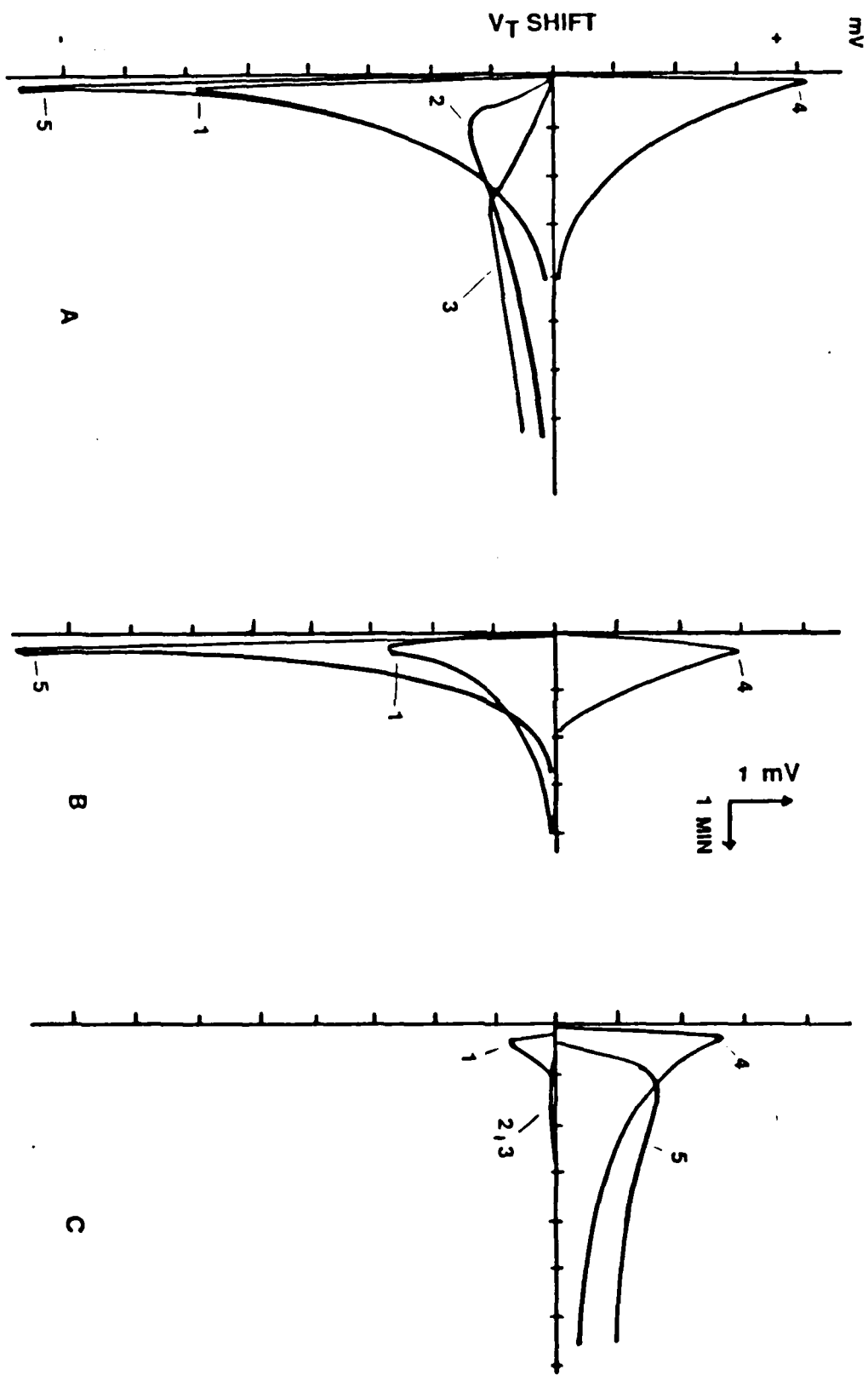


Fig. 6

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 413 800 N. Quincy Street Arlington, Virginia 22217	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 5042 Crane, Indiana 47522	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Washington, D.C. 20360	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
DTNSRDC Attn: Dr. G. Bosmajian Applied Chemistry Division Annapolis, Maryland 21401	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 92132	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1		

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. Paul Delahay
Department of Chemistry
New York University
New York, New York 10003

Dr. P. J. Hendra
Department of Chemistry
University of Southampton
Southampton SO9 5NH
United Kingdom

Dr. J. Driscoll
Lockheed Palo Alto Research
Laboratory
3251 Hanover Street
Palo Alto, California 94304

Dr. D. N. Bennion
Department of Chemical Engineering
Brigham Young University
Provo, Utah 84602

Dr. R. A. Marcus
Department of Chemistry
California Institute of Technology
Pasadena, California 91125

Dr. J. J. Auborn
Bell Laboratories
Murray Hill, New Jersey 07974

Dr. Joseph Singer, Code 302-1
NASA-Lewis
21000 Brookpark Road
Cleveland, Ohio 44135

Dr. P. P. Schmidt
Department of Chemistry
Oakland University
Rochester, Michigan 48063

Dr. Manfred Breiter
Institut für Technische Elektrochemie
Technischen Universität Wien
9 Getreidemarkt, 1160 Wien
AUSTRIA

Dr. E. Yeager
Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 44106

Dr. C. E. Mueller
The Electrochemistry Branch
Naval Surface Weapons Center
White Oak Laboratory
Silver Spring, Maryland 20910

Dr. Sam Perone
Chemistry & Materials
Science Department
Lawrence Livermore National Laboratory
Livermore, California 94550

Dr. Royce W. Murray
Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27514

Dr. B. Brummer
EIC Incorporated
111 Downey Street
Norwood, Massachusetts 02062

Dr. Adam Heller
Bell Laboratories
Murray Hill, New Jersey 07974

Dr. A. B. Ellis
Chemistry Department
University of Wisconsin
Madison, Wisconsin 53706

Library
Duracell, Inc.
Burlington, Massachusetts 01803

Electrochimica Corporation
20 Kelly Court
Menlo Park, California 94025-1418

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. M. Wrighton
Chemistry Department
Massachusetts Institute
of Technology
Cambridge, Massachusetts 02139

Dr. B. Stanley Pons
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

Donald E. Mains
Naval Weapons Support Center
Electrochemical Power Sources Division
Crane, Indiana 47522

S. Ruby
DOE (STOR)
Room 5E036 Forrestal Bldg., CE-14
Washington, D.C. 20595

Dr. A. J. Bard
Department of Chemistry
University of Texas
Austin, Texas 78712

Dr. Janet Osteryoung
Department of Chemistry
State University of New York
Buffalo, New York 14214

Dr. Donald W. Ernst
Naval Surface Weapons Center
Code R-33
White Oak Laboratory
Silver Spring, Maryland 20910

Mr. James R. Moden
Naval Underwater Systems Center
Code 3632
Newport, Rhode Island 02840

Dr. Bernard Spielvogel
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709

Dr. Aaron Fletcher
Naval Weapons Center
Code 3852
China Lake, California 93555

Dr. M. M. Nicholson
Electronics Research Center
Rockwell International
3370 Miraloma Avenue
Anaheim, California

Dr. Michael J. Weaver
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Dr. R. David Rauh
EIC Laboratories, Inc.
111 Downey Street
Norwood, Massachusetts 02062

Dr. Aaron Wold
Department of Chemistry
Brown University
Providence, Rhode Island 02192

Dr. Martin Fleischmann
Department of Chemistry
University of Southampton
Southampton SO9 5NH ENGLAND

Dr. R. A. Osteryoung
Department of Chemistry
State University of New York
Buffalo, New York 14214

Dr. John Wilkes
Air Force Office of Scientific
Research
Bolling AFB
Washington, D.C. 20332

Dr. R. Nowak
Naval Research Laboratory
Code 6171
Washington, D.C. 20375

Dr. D. F. Shriver
Department of Chemistry
Northwestern University
Evanston, Illinois 60201

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. Hector D. Abruna
Department of Chemistry
Cornell University
Ithaca, New York 14853

Dr. A. B. P. Lever
Chemistry Department
York University
Downsview, Ontario M3J1P3

Dr. Stanislaw Szpak
Naval Ocean Systems Center
Code 633, Bayside
San Diego, California 95152

Dr. Gregory Farrington
Department of Materials Science
and Engineering
University of Pennsylvania
Philadelphia, Pennsylvania 19104

M. L. Robertson
Manager, Electrochemical
and Power Sources Division
Naval Weapons Support Center
Crane, Indiana 47522

Dr. T. Marks
Department of Chemistry
Northwestern University
Evanston, Illinois 60201

Dr. Micha Tomkiewicz
Department of Physics
Brooklyn College
Brooklyn, New York 11210

Dr. Lesser Blum
Department of Physics
University of Puerto Rico
Rio Piedras, Puerto Rico 00931

Dr. Joseph Gordon, II
IBM Corporation
5600 Cottle Road
San Jose, California 95193

Dr. Nathan Lewis
Department of Chemistry
Stanford University
Stanford, California 94305

Dr. D. H. Whitmore
Department of Materials Science
Northwestern University
Evanston, Illinois 60201

Dr. Alan Bewick
Department of Chemistry
The University of Southampton
Southampton, SO9 5NH ENGLAND

Dr. E. Anderson
NAVSEA-56Z33 NC #4
2541 Jefferson Davis Highway
Arlington, Virginia 20362

Dr. Bruce Dunn
Department of Engineering &
Applied Science
University of California
Los Angeles, California 90024

Dr. Elton Cairns
Energy & Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Dr. Richard Pollard
Department of Chemical Engineering
University of Houston
Houston, Texas 77004

Dr. M. Philpott
IBM Corporation
5600 Cottle Road
San Jose, California 95193

Dr. Donald Sandstrom
Boeing Aerospace Co.
P.O. Box 3999
Seattle, Washington 98124

Dr. Carl Kannewurf
Department of Electrical Engineering
and Computer Science
Northwestern University
Evanston, Illinois 60201

Dr. Joel Harris
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. Robert Somoano
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California 91103

Dr. Johann A. Joebstl
USA Mobility Equipment R&D Command
DRDME-EC
Fort Belvoir, Virginia 22060

Dr. Judith H. Ambrus
NASA Headquarters
M.S. RTS-6
Washington, D.C. 20546

Dr. Albert R. Landgrebe
U.S. Department of Energy
M.S. 6B025 Forrestal Building
Washington, D.C. 20595

Dr. J. J. Brophy
Department of Physics
University of Utah
Salt Lake City, Utah 84112

Dr. Charles Martin
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Dr. H. Tachikawa
Department of Chemistry
Jackson State University
Jackson, Mississippi 39217

Dr. Theodore Beck
Electrochemical Technology Corp.
3935 Leary Way N.W.
Seattle, Washington 98107

Dr. Farrell Lytle
Boeing Engineering and
Construction Engineers
P.O. Box 3707
Seattle, Washington 98124

Dr. Robert Gotscholl
U.S. Department of Energy
MS G-226
Washington, D.C. 20545

Dr. Edward Fletcher
Department of Mechanical Engineering
University of Minnesota
Minneapolis, Minnesota 55455

Dr. John Fontanella
Department of Physics
U.S. Naval Academy
Annapolis, Maryland 21402

Dr. Martha Greenblatt
Department of Chemistry
Rutgers University
New Brunswick, New Jersey 08903

Dr. John Wasson
Syntheco, Inc.
Rte 6 - Industrial Pike Road
Gastonia, North Carolina 28052

Dr. Walter Roth
Department of Physics
State University of New York
Albany, New York 12222

Dr. Anthony Sammells
Eltron Research Inc.
4260 Westbrook Drive, Suite 111
Aurora, Illinois 60505

Dr. C. A. Angell
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Dr. Thomas Davis
Polymer Science and Standards
Division
National Bureau of Standards
Washington, D.C. 20234

Ms. Wendy Parkhurst
Naval Surface Weapons Center R-33
R-33
Silver Spring, Maryland 20910

DL/413/83/01
359/413-2

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. John Owen
Department of Chemistry and
Applied Chemistry
University of Salford
Salford M5 4WT ENGLAND

Dr. Boone Owens
Department of Chemical Engineering
and Materials Science
University of Minnesota
Minneapolis, Minnesota 55455

Dr. J. O. Thomas
University of Uppsala
Institute of Chemistry
Box 531
S-751 21 Uppsala, Sweden

Dr. O. Stafsudd
Department of Electrical Engineering
University of California
Los Angeles, California 90024

Dr. S. G. Greenbaum
Department of Physics
Hunter College of CUNY
New York, New York 10021

Dr. Menahem Anderman
W.R. Grace & Co.
Columbia, Maryland 20144

END

DATE

FILMED
7-88

DTIC